

Electrochemical performance of nanocrystalline lead oxide in VRLA batteries

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Abstract

Nanocrystalline lead oxide was prepared through two-step chemical reactions and has been tested as the electrode active material for the valve-regulated lead acid (VRLA) battery. By using this nanocrystalline lead oxide, the pasted electrodes can be directly formatted without a curing process. The initial specific capacity of the new electrode was 30% higher than that of the electrode with the conventional ball-milled lead oxide and the cycle behaviour of the new electrode was also improved. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Nanocrystalline; Lead/acid battery; Lead oxide; Curing; Formation; Specific capacity

1. Introduction

Lead oxide is the basic material of the electrode active mass in lead-acid batteries. The two predominant production methods used to produce lead oxide are the ‘ball-mill’ and the ‘Barton-pot’ method [1]. The lead oxide manufactured by the ball-mill process is almost 100% tetragonal (α -PbO) while that produced by the Barton (molten metal) system can contain varying and controlled ratios of α -PbO: β -PbO depending on the temperature during the process [2,3]. The crystal structure of PbO is of significant interest with respect to the plate making processes [4]. In the conventional manufacturing processes of lead acid batteries it is necessary to allow for a plate curing process after pasting the plates. The curing process consists of the oxidation of the free lead in the plates to a level below 5 wt.%, conversion of the wet pasted plates to a dry, crackfree, uniform plate, having sufficient strength and adhesion to the grid. A free lead content of more than 5% is supposed to cause difficulties during formation of positive plates (swelling or warping or extensive sludge formation). However, the curing process has to be done under rigidly controlled condition of temperature and humidity and it is also time consuming and costly [5,6].

There is a growing trend towards the use of pure lead monoxide for the production of positive plates. The advantage of using the pure lead oxide is that it can eliminate the lead oxidation step and therefore significantly reduce the curing time and the processing cost [3].

In recent years, nanostructured materials have been of interest because they are distinguished from conventional polycrystalline materials by the size of the crystalline that compose them [7–9]. Results show that the nanocrystalline materials have remarkable electrochemical performance, high specific capacity and good cycle behaviour.

The objectives of this study are to develop a chemical procedure to synthesise a nanocrystalline pure lead oxide (α -PbO), to use this pure α -PbO as the positive active mass of lead acid electrode and to evaluate its electrochemical performance under a non-curing process in the test cell.

2. Experimental

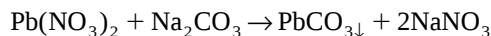
2.1. Material preparation

Nanocrystalline α -PbO was prepared by two chemical reaction steps. The first reaction was carried out in a flask, containing 500 ml of 0.5 M $\text{Pb}(\text{NO}_3)_2$ (Aldrich) solution. A 550-ml volume of 0.5 M aqueous Na_2CO_3 (Aldrich)

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solution was then added slowly to the $\text{Pb}(\text{NO}_3)_2$ solution from a burette. The solution was stirred constantly by a magnetic stirrer. The chemical reaction in the solution is given by the following equation:



Completion of the reaction resulted in the formation of a white PbCO_3 precipitate, which was then filtered and washed several times with distilled water to remove Na^+ and NO_3^- , then dried at 110°C in an air oven. The dried fine powder was calcined at 320°C in air for 4 h. The white PbCO_3 powder was decomposed and yielded a yellow-coloured powder, which was then characterised by a X-ray diffractometer (Philips P W 1730 with a $\text{Cu K}\alpha$ radiation) as $\alpha\text{-PbO}$. For comparison, a ball-milled leady oxide (supplied by the Shenyang Battery Co., China) was also tested as a reference sample. Specific surface area of the two oxides was measured by a Surface Area and Porosimetry Analyzer (Tristar 3000) with liquid nitrogen.

2.2. Paste and electrode preparation

Positive pastes prepared from two formulae are given in Table 1.

The required amount of the two oxides was placed in two containers, the required amount of water was added, then acid was introduced at a slow rate and with good dispersion over the paste. The amount of water added could be slightly modified to obtain the required density. The plates were obtained by applied the paste evenly by hand to a lead-coated glass fibre grid with dimensions of $50\text{ mm} \times 45\text{ mm}$. The plate thickness was 1.2 mm.

The plates pasted with ball-milled oxide were mounted vertically in a stainlesssteel rack, placed in a glass container, and then put into a water bath where the temperature was controlled at 50°C with relative humidity $>95\%$. The curing was conducted for 48 h. After curing, the plates were dried at 60°C for 24 h. The paste weight was 10 g/plate.

2.3. Battery assembly and test

The positive plate prepared from synthesised $\alpha\text{-PbO}$ was assembled in test cells directly without a curing process. Each positive plate (the cured plate with the ball-milled

oxide and the non-cured plate with the synthesised oxide) was sandwiched between two commercial negative plates (from commercial batteries) and with separators (absorptive glass-mat, AGM) in between. The sandwiched electrodes were inserted into a commercial battery case under a compress of 50 kPa. Two separate polycarbonate fixing sheets were inserted into each cell within the battery case to provide the plate compression. An amount of electrolyte of H_2SO_4 (1.23 relative density) equivalent to 15 cm^3 per Ah was added and the total cell volumes were held constant (plates, separator and electrolyte). The cell was then sealed and a rubber valve was fixed to it. After 2 h of plate soaking, the cell formation was started with a constant formation current density of 10 mA cm^{-2} for 24 h (with 1-h step and 10-min rest programmed). Since the negative electrode had a capacity larger than that of the positive electrode, the cell capacity was restricted by the capacity of the positive electrode. After formation, the reserved capacity of the cell was recorded at a constant current density of 10 mA cm^{-2} until the terminal voltage fell to 1.75 V. The product of the current and the time yielded the first discharge capacity, which was used as an indication of the formation condition of the plate. The charging and discharging cycle tests were then started at the same constant current density. During charging a constant current was maintained until the cell voltage reached to 2.45 V. The charging process was then held at this voltage until 110% of the previous discharge capacity was reached. The ratio of the measured capacity to the theoretical capacity of positive active material (PAM) can be used to define the PAM utilisation.

The charge/discharge sequence was repeated for 50 cycles. The formation and the cycling tests were carried out with an ARBIN cycler (BT4^+).

Samples of leady oxide and paste, cured and formed materials were subjected to X-ray diffraction (XRD) phase analysis. The morphology of the materials was examined using scanning electron microscopy (SEM). The particle size distribution was measured by using a mastersizer (MSS Model, Malvern, UK). The free lead contents of oxides and the paste composition were analysed by using both gravimetric method and XRD phase analysis methods.

3. Results and discussion

Fig. 1 shows the XRD patterns of the synthesised and the ball-milled oxides. The reflections of the synthesised lead oxide correspond very well to the theoretical $\alpha\text{-PbO}$ pattern (ASTM 05-0561). The difference between the ball-milled leady oxide and the synthesised $\alpha\text{-PbO}$ represents the free lead in the ball-mill oxide. The average crystallite size of the oxide can be calculated by using the Traces Program [10] according to the Scherrer formula:

$$\text{crystallite size } d = K\lambda/\beta\cos\theta$$

Table 1
Paste formulae

Ingredient	Synthesised pure $\alpha\text{-PbO}$ paste	Ball-milled paste
Noncrystalline $\alpha\text{-PbO}$ (g)	100	
Ball-milled PbO (g)		100
Fibres (g)	0.2	0.2
Water (cm^3)	15	15
H_2SO_4 , 1.4 specific gravity (sp.g) (cm^3)	9.5	9.5
Density (g cm^{-3})	4.0	4.0

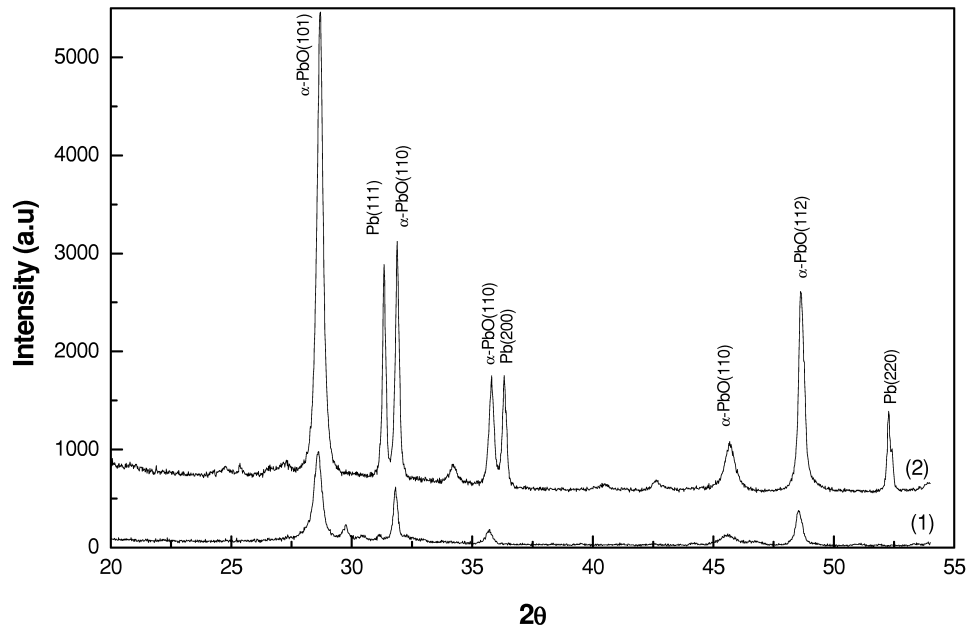


Fig. 1. X-Ray diffraction patterns of (1) synthesised α -PbO, and (2) ball-milled leady oxide.

The average crystallite size of the synthesised α -PbO is around 23 nm, while the average crystallite size of the ball milled oxide is around 220 nm.

SEM images of the synthesised α -PbO and ball-milled oxide are shown in Fig. 2. Compared with the ball-milled oxide, the synthesised α -PbO powders are more homogenous and the grain size is around 100–300 nm, which is much smaller than that of the ball-milled oxide (1–10 μm). Physical properties of the ball-milled oxide and synthesised α -PbO are listed in Table 2. The median diameter of synthesised α -PbO particles examined by the Laser Particle Size Distribution (Mastersizer, UK) is about one order of magnitude smaller than that of the ball-milled

material. The phase composition data from gravimetric analysis, the acid absorption data from titration and the specific surface area data from Brunauer–Emmett–Teller (BET) measurement, respectively.

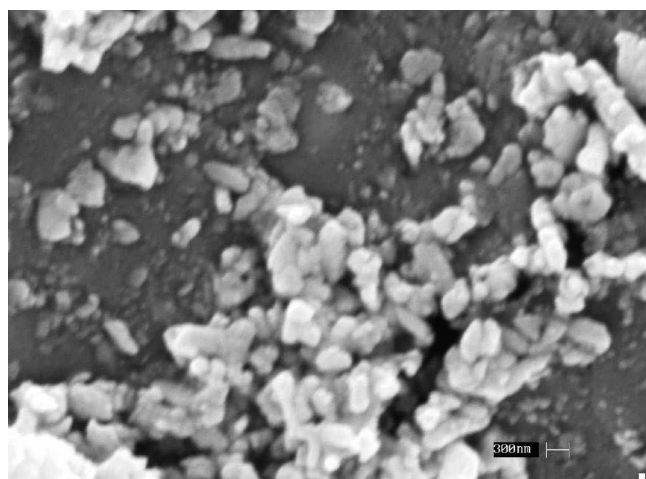
Table 3 gives the results of X-ray examination on the plates before and after formation. The XRD phase analysis shows that the non-cured plate prepared with the pure α -PbO paste contains higher level 3BS ($3\text{PbO} \cdot \text{H}_2\text{O} \cdot \text{PbSO}_4$) than that of cured plate prepared with ball-milled paste. After formation, the composition of two pastes becomes similar. This indicates that the plate with synthesised α -PbO can be formatted just as well as the plate with ball-milled and cured paste, even without curing. The

Table 2
Physical properties of ball-milled leady oxide and synthesised pure α -PbO

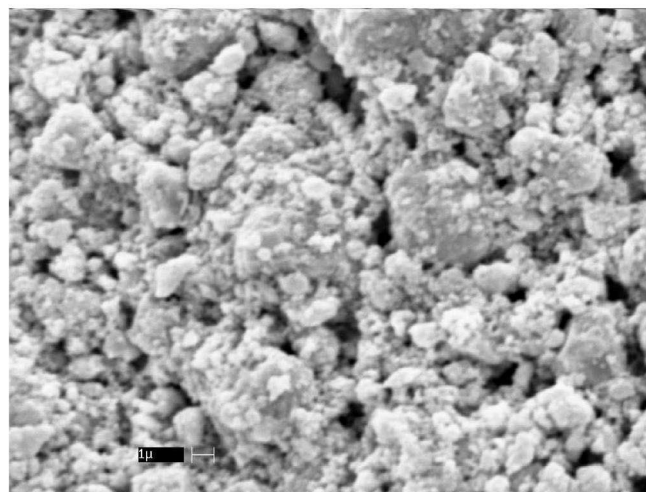
	Ball-milled leady oxide	Synthesised α -PbO
Phase composition (wt., %)		
Free Pb	20.5	—
α -PbO	79.5	100
Particle median diameter (μm)	7.74	0.53
Specific surface area BET ($\text{m}^2 \text{g}^{-1}$)	1.48	2.85
Acid absorption ($\text{mg H}_2\text{SO}_4/\text{g oxide}$)	220	270

Table 3
X-Ray analysis of paste composition (wt.%) before and after formation

Paste	Before formation				After formation		
	Pb	α -PbO	β -PbO	3BS	α -PbO ₂	β -PbO ₂	PbSO ₄
Ball milled (cured)	3.50	62.20	0.98	23.50	9.10	75.50	15.50
Synthesised α -PbO (non-cured)	0	41.58	11.41	47.07	10.94	78.48	10.38



(a)



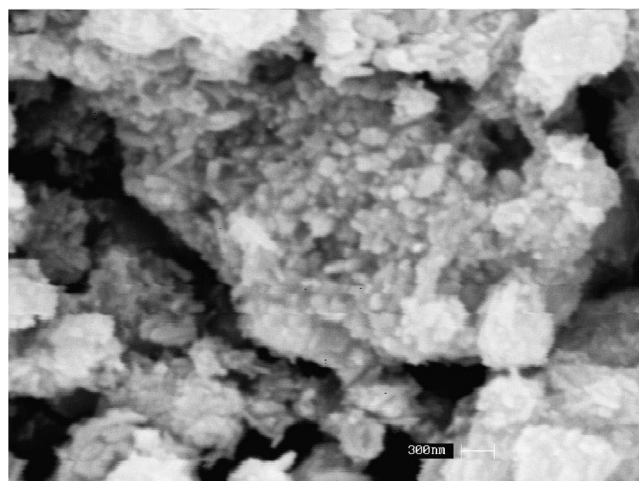
(b)

Fig. 2. SEM images of (1) synthesised α -PbO, and (2) ball-milled leady oxide.

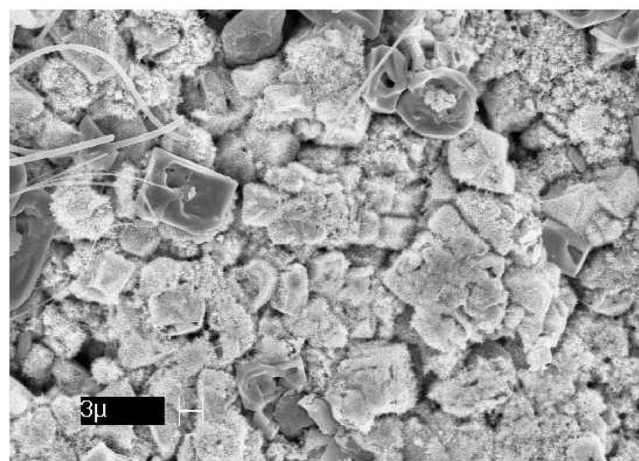
reason for the high level of 3BS produced with synthesised α -PbO under the same paste mixing condition is not known but may be attributed to the fine particles and its high reactivity with sulfuric acid. SEM images of the two plates just after formation are shown in Fig. 3.

The first discharge capacity of the test cell was recorded after formation, and was used for the evaluation of the plate formation. The measured discharge capacity vs. the cycle number is given in Fig. 4, which shows that the first discharge capacity of the synthesised α -PbO is 30% higher than that of the ball-milled one. The high initial discharge capacity of synthesised α -PbO can be attributed to its fine particle size. This result also indicates that the plate with the synthesised α -PbO can be well formatted even without a plate curing process.

It was thought that the using of too fine grain powder may be unfavourable to the life cycle of the electrode,



(a)



(b)

Fig. 3. SEM images of the surface of the positive plate just after formation: (a) prepared with synthesised α -PbO, and (b) prepared with ball-milled oxide.

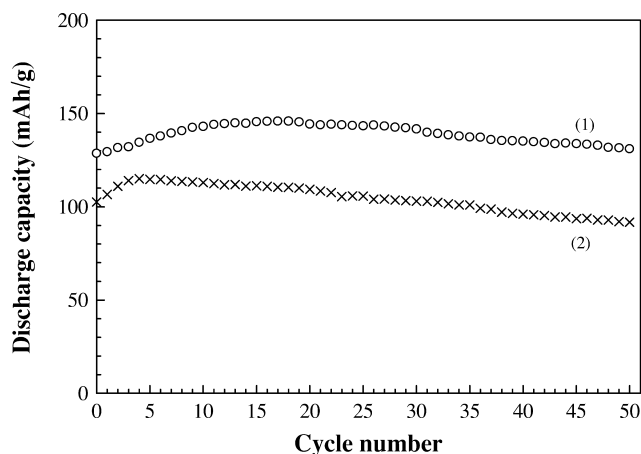
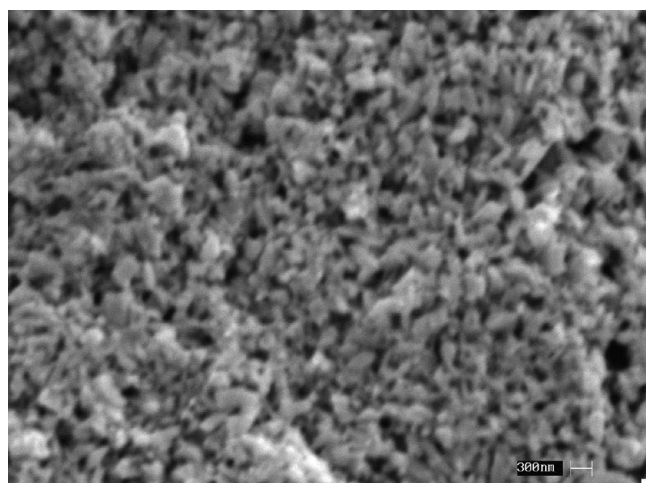
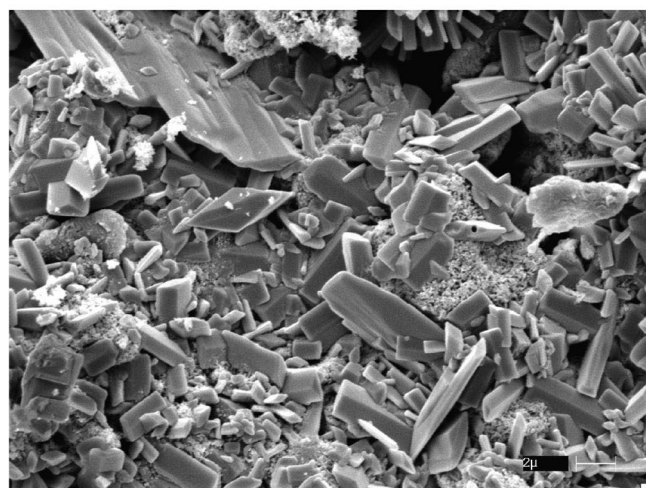


Fig. 4. Discharge capacity vs. cycle number for (1) test cell with synthesised α -PbO, and (2) test cell with ball-milled leady oxide.



(a)



(b)

Fig. 5. SEM images of the surface of the positive plate after 50 cycles: (a) prepared with synthesised α -PbO, and (b) prepared with ball-milled oxide.

however, the cycle performance up to 50 cycles of the test cell with the synthesised α -PbO was even better than the cell with the ball-milled conventional cured material. After 50 cycles, each positive plate from both testing cells was took out, washed and dried in a vacuum furnace. Both of the two plates were in a good condition. SEM images of

the two plates after 50 cycles are shown in Fig. 5. Morphology of the conventional cured plate after cycle (in discharge condition) shows well-defined crystals of PbSO_4 (Fig. 5b), while the crystals of the synthesised plate are much smaller and more homogeneous (Fig. 5a). The active material of the plate (Fig. 5a), appears more concrete and compressed than the plate prepared with ball-mill oxide (Fig. 5b). This may be attributed to a comparative small volume change of the synthesised plate during cycling and would be favourable to the cycle life of the plate.

4. Conclusion

Nanocrystalline α -PbO has been synthesised by a simple chemical method. This material demonstrates several advantages over the conventional ball-milled lead oxide when tested as the positive electrode material. Using the synthesised α -PbO, the plate can be directly formatted without a curing process. The initial specific capacity of the test cell with the new electrode was 30% higher than that of the electrode with the conventional ball-milled leady oxide. The non-curing process could greatly simplify the plate making procedure and significantly reduces the processing cost. The cycle behaviour of the new electrode within the test period was improved. However, further exploration of the cycle performance of the synthesised plate and prolonged cycle life testing is still needed.

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